at 7.24 dd (6, 2.5, H-17), 5.98 dd (6, 2, H-16), 5.28 (H-19), 0.96 (C-4 methyl), 0.78 d (7, six protons, isopropyl), and 0.60 ppm (C-10 methyl)] gave exclusively **2a**, 85%, infrared bands at 3470 and 1765 cm^{-1}, no vinyl protons, 0.98 d and 0.88 d (7, isopropyl), 0.79, and 0.75 ppm (C-4 and C-10 methyls).

However, photolysis (Pyrex filter) of **1b**, λ_{max}(ethanol) 237.5 and 295 mμ (ϵ_{max} 11200 and 112), infrared bands at 1750, 1680, and 1600 cm^{-1}, relevant nmr signals at 5.19 br (H-19), 5.02 (H-16), 1.11 (C-4 methyl), 0.82 d (7, six protons, isopropyl), and 0.59 ppm (C-10 methyl), took an unexpected and unprecedented course yielding only 20% of **2b**, infrared bands at 1770 and 1750 cm^{-1}, no vinyl protons, 1.05 d and 1.02 d (6, isopropyl), 1.12 (C-4 methyl), and 0.77 ppm (C-10 methyl), 15% of recovered **1b**, and 60% of a new isomer whose physical properties indicated retention of the cyclopentenone chromophore, λ_{max} 247 and 290 mμ (ϵ_{max} 12500 and 170), infrared bands at 1750, 1675, and 1600 cm^{-1}, nmr singlet at 5.27 (H-16), disappearance of the bridge double bond and disappearance of the methyl group at C-10 [only one methyl singlet at 1.24 (C-4 methyl), methyl doublets at 0.82 and 0.70 ppm (7, isopropyl)]. The only structure which satisfies these properties is **3**.

Further photolysis (no Pyrex filter) of **3** furnished a third completely saturated isomer (65%, infrared bands at 1775 and 1750 cm^{-1}, no vinyl protons) which must be assigned formula **4** because of the appearance in the nmr spectrum of a doublet of doublets at 4.18 ppm (H-17) and the retention of the C-4 methyl singlet (1.26 ppm) and the methyl doublets (0.87 and 0.84 ppm) of the isopropyl group.[5]

Lack of deuterium incorporation when the various photolyses were carried out in CH_3OD precluded an ionic reaction involving intermolecular H^+ transfer. From the absence of products characteristic of hydrogen abstraction from solvents methanol and cyclohexane, it then followed that hydrogen transfers during reactions b and c were completely intramolecular. Since, as in all compounds of this type, the π-electron system of the *endo*-α,β-unsaturated ketone chromophore is close to the π-electron system of the isolated double bond which in turn strongly shields the C-10 methyl groups we infer that the conversion of **1b** to **3** has its origin in internal photosensitization of the isolated double bond by the conjugated chromophore of **1**.[6] Intramolecular hydrogen abstraction from the C-10 methyl group by the resulting diradical is accompanied or followed by a formal hydrogen migration from C-19 to C-18[7] and ring closure to **3**.[10]

At first glance it seemed tempting to ascribe this unusual internal photosensitization to the n → π* triplet of the cyclopentenone chromophore and to assume that reaction c, which occurs only at $\lambda < 300$ mμ, involves the π–π* triplet, although it requires hydrogen abstraction. The effect of the methoxyl group in promoting reaction b at the expense of reaction a by sensitizing the double bond could then be understood in terms of its presumed[11] influence in raising the energy of the **1b** n → π* triplet relative to the ground state, although the magnitude of the effect seemed surprising.

This was contraindicated by the emission spectra.[12] That of **1a** exhibited the highly structured phosphorescence spectrum characteristic of emission from n → π* triplets (0–0 band 74.5 kcal),[13] whereas the entirely featureless phosphorescence spectra of **1b** and **3** which begin at 74 kcal are indicative of π → π* triplets.[14,15] Efforts to shed light on the actual mechanism and to clarify related aspects are in progress.

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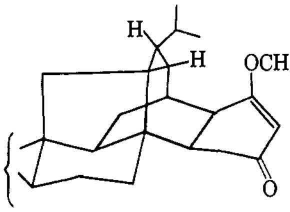
(5) Photolysis of **3** with a Pyrex filter resulted in quantitative recovery of starting material. Photolysis of **1b** without a filter gave **2b** and **4**, the latter being formed from **3** as shown by analysis of aliquots taken at intermediate periods. Since the relative amount of **2b** seemed to decrease with time, the photolysis of **2b** (Pyrex filter) was studied separately. This established that **2b** was in equilibrium with **1b** which in turn was converted to **3**.

(6) The *cis–trans* isomerization of certain olefins reported by H. Morrison (*Tetrahedron Letters*, 3653 (1964); *J. Am. Chem. Soc.*, **87**, 931 (1965)) provides a precedent of sorts.

(7) Since evidence for direct 1,2-hydrogen shifts is meager,[8] we are considering the possibility that H-19 is passed to C-18 *via* C-16 or C-17.[9]

(8) R. Kh. Freidlina, *Advan. Free-Radical Chem.*, 1, 215 (1965); however, see R. E. K. Winter and R. F. Lindauer, *Tetrahedron Letters*, **25**, 2345 (1967); G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Close, *J. Am. Chem. Soc.*, **87**, 1410 (1965); D. I. Schuster and I. S. Krull, *ibid.*, **88**, 3456 (1966); A. Padwa, D. Crumrine, R. Hartman, and R. Layton, *ibid.*, **89**, 4435 (1967).

(9) Alternate formulations **5** and **6** (for **3** and **4**, respectively), which would avoid this difficulty, are rejected because of the large distance required for hydrogen transfer from the C-10 methyl to C-18 (~4 A in Dreiding models of **2b**) and from C-19 to C-17 of **5** (~3.8 A) and because **6** cannot be constructed with the models. It seems unreasonable to suppose that bond distortions in the photoexcited states could reduce these distances sufficiently. The possibility of resolving this ambiguity by X-ray analysis is being investigated.



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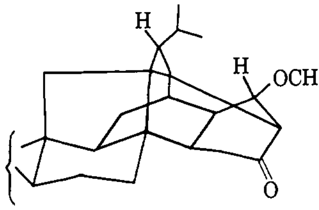

6

(10) For other examples of photochemically induced hydrogen transfers to double bonds in bridged compounds, see A. M. Parsons and D. J. Moore, *J. Chem. Soc., Sect. C*, 2026 (1966); H. D. Scharf, *Tetrahedron*, **23**, 3057 (1967).

(11) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962); H. E. Zimmerman, *Pure Appl. Chem.*, **9**, 493 (1964); H. E. Zimmerman, L. D. Rieke, and J. R. Scheffer, *J. Am. Chem. Soc.*, **89**, 2033 (1967).

(12) Kindly determined by Mrs. Frances DeTar at 77°K in EPA glass.

(13) (a) V. Ermolaev and A. Terenin, *Opt. i Spektroskopiya*, 1, 523 (1956); (b) M. Kasha, *Radiation Res. Suppl.*, 2, 265 (1960).

(14) This appears to be the first demonstration of phosphorescence in a cyclopentenone (private communication from Professor P. de Mayo). See also E. Y. Y. Lam, D. Valentine, and G. S. Hammond, *J. Am. Chem. Soc.*, **89**, 3482 (1967).

(15) In view of the close structural similarity of **1a** and **1b**, the cautionary note expressed by H. E. Zimmerman and J. S. Swenton, *J. Am. Chem. Soc.*, **89**, 906 (1967), is probably not applicable here. See also G. Porter and P. Suppan, *Proc. Chem. Soc.*, 191 (1964); *Pure Appl. Chem.*, **9**, 499 (1964), for a discussion of the effect of electron-donating groups on lowering the energy of the π → π* triplet.

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Thexylborane as a Convenient Reagent for the Cyclic Hydroboration of Dienes. Stereospecific Syntheses *via* Cyclic Hydroboration

Sir:

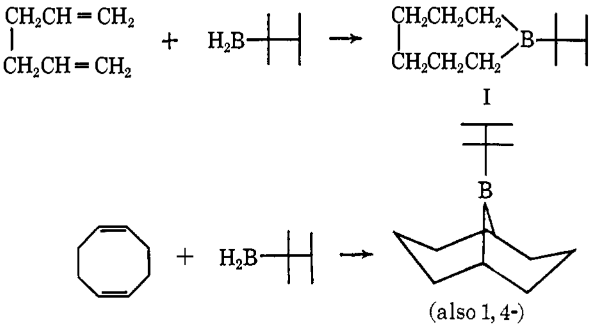
The simultaneous addition of equimolar quantities of thexylborane (2,3-dimethyl-2-butylborane) and appro-

Table I. Reaction of Thexylborane with Diene in the Ratio Required for Monohydroboration[a]

Diene	Time,[b] hr	Residual diene, mmoles	Hydroboration, % Non	Mono	Di	Residual hydride, mmoles
1,4-Pentadiene	4	13.6	45	9	46	0.1
1,5-Hexadiene	4	13.6	45	9	46	0.0
1,7-Octadiene	4	9.3	31	38	31	0.6
1,4-Cyclohexadiene	24	2.9	10	81	9	2.3
1,5-Cyclooctadiene	4	14.5	48	3	49	0.0
4-Vinylcyclohexene	4	12.0	40	20	40	0.2
D-(+)-Limonene	4	15.0	50	0	50	1.2

[a] Diene, 30 mmoles, and 15 mmoles of thexylborane, each in 30 ml of tetrahydrofuran, were added simultaneously by means of a Sage constant-addition syringe pump to 60 ml of rapidly stirred tetrahydrofuran over 2.5 hr. [b] After addition of reagents had been completed.

priate dienes to tetrahydrofuran (dilute solution technique) produces excellent yields of the corresponding cyclic and bicyclic derivatives (I, II).



(also 1,4-)

II

This procedure makes cyclic and bicyclic organoboranes of definite structure readily available under mild conditions[1] from appropriate dienes and makes it possible to utilize their unique structures and properties for synthetic purposes.[2]

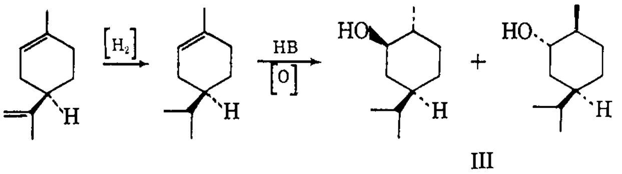
Previously we had observed that the hydroboration–oxidation of certain dienes results in the formation of unexpected products, such as the predominant formation of the 1,4-diol, instead of the expected 1,5-diol, from 1,4-pentadiene.[3] We deduced that cyclic hydroboration must be intervening to cause the anomalous product formation, and circumvented it by use of the monofunctional hydroborating agent, disiamylborane.[4] Since then it has become apparent that control of the hydroboration reaction to achieve cyclic hydroboration could provide a most valuable addition to the possibilities for the hydroboration reaction.

The unique ability of thexylborane to react under the dilute solution technique with appropriate dienes to give cyclic derivatives is indicated by the data in Table I. In these experiments 0.5 M solutions of thexylborane and 1.0 M solutions of the diene (in the ratio for complete monohydroboration) were added simultaneously over 2.5 hr to rapidly stirred tetrahydrofuran at 0°. If the reaction were to involve a selective monohydroboration, then the product would consist of 0% residual diene, 100% monohydroboration product, and 0% dihydroboration product (identifiable as monools and diols after oxidation). Statistical hydroboration of the diene should produce 25% residual diene, 50% monohydroboration product, and 25% dihydroboration product. On the other hand, quantitative cyclic hydroboration would result in the formation of 50% residual diene, 0% monohydroboration product, and 50% dihydroboration product.

The data reveal that under these mild conditions 1,4-cyclohexadiene undergoes preferential monohydroboration.[5] Evidently the conversion of the monohydroboration product into the 7-borabicyclo[2.2.1]heptane structure involves too much strain to be achieved under these mild conditions. On the other hand, 1,5-cyclooctadiene is evidently readily converted into the bicyclic derivatives. (Both 1,4- and 1,5-bicyclic derivatives are formed.) The reaction of 1,7-octadiene indicates an approach to statistical hydroboration, with the possible formation of only moderate amounts of cyclic derivatives. On the other hand, 1,4-pentadiene, 1,5-hexadiene, 4-vinylcyclohexene, and D-(+)-limonene all indicate that cyclic hydroboration is the dominant reaction path.

The value of this new approach is indicated by the following stereospecific conversion of D-(+)-limonene into essentially pure D-(−)-(1*S*,2*R*,4*R*)-limonene-2,9-diol ("*m-cis* diol") or into essentially pure D-(−)-carvomenthol.

The simple hydroboration–oxidation of dihydrolimonene[6] leads to a 61:39 mixture of two isomers (III), exceedingly difficult to separate.



III

Similarly, the usual dihydroboration–oxidation of limonene leads to a complex mixture of isomeric diols. However, oxidation of the reaction product from the cyclic hydroboration of D-(+)-limonene yielded essentially pure D-(−)-(1*S*,2*R*,4*R*)-limonene-2,9-diol. Similarly, by selective protonolysis of the primary carbon–boron bond with acetic acid, the bicyclic intermediate can be converted into essentially pure D-(−)-carvomenthol (IV).

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(1) Numerous heterocyclic organoboranes have been synthesized by R. Köster in the course of his fascinating studies of the transformations of organoboranes at elevated temperatures: R. Köster, *Angew. Chem. Intern. Ed. Engl.*, **3**, 174 (1964). However, this approach is not generally suitable for the synthesis of specific structures, especially structures containing functional substituents.

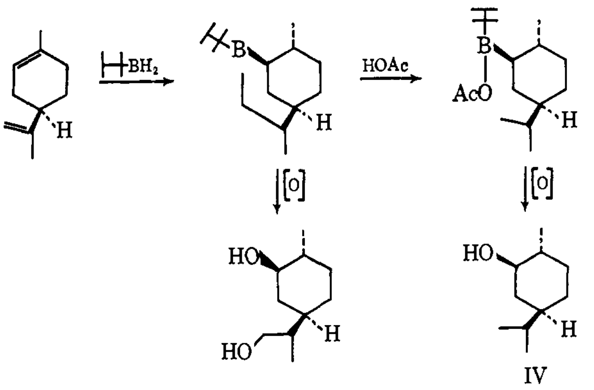
(2) The present communication describes the utilization of such cyclic hydroboration for stereospecific syntheses. The following communication (H. C. Brown and E. Negishi, *J. Am. Chem. Soc.*, **89**, 5477 (1967) will indicate the application of such cyclic hydroboration to the synthesis of cyclic and bicyclic ketones.

(3) G. Zweifel, K. Nagase, and H. C. Brown, *ibid.*, **84**, 183 (1962).

(4) G. Zweifel, K. Nagase, and H. C. Brown, *ibid.*, **84**, 190 (1962).

(5) Compare G. Zweifel and H. C. Brown, *ibid.*, **85**, 2066 (1963).

(6) W. F. Newhall, *J. Org. Chem.*, **23**, 1274 (1958); C. A. Brown and H. C. Brown, *J. Am. Chem. Soc.*, **84**, 2829 (1962).



Twenty milliliters each of 1.5 *M* D-(+)-limonene (bp 171–173° (743 mm), n^{20}D 1.4724, αD +99°) and thexylborane[5] were simultaneously added to 50 ml of tetrahydrofuran at 0° over 1 hr. After oxidation with alkaline hydrogen peroxide, the aqueous phase was saturated with potassium carbonate. Distillation yielded the diol, bp 152–155° (4.8 mm),[6] converted to the diacetate, bp 143–145° (5 mm). Examination of the diacetate by glpc (polyphenyl ether column) revealed a minimum 92% yield of the "*m-cis*" diol, with only trace amounts of the "*m-trans*" present.

Following preparation of the cyclic intermediate as above, 90 ml of anhydrous acetic acid was added,[7] tetrahydrofuran was distilled off until the temperature in the flask reached 110°, and the temperature was maintained there for 12 hr. Oxidation produced 3.59 g, 75% yield, of D-(−)-carvomenthol,[8] bp 85–88° (0.4 mm), n^{20}D 1.4609, [α]D −23.0° (*c* 16, CCl$_4$). Glpc examination revealed the absence of D-(+)-isocarvomenthol.

It is evident that this approach provides a new, simple procedure to achieve stereochemical control of the direction of hydroboration and of the many derivatives into which organoboranes can be converted. We are also exploring the possibility of achieving similar control by the introduction of a suitable temporary "anchor" for the hydroborating agent.

[7] The selective protonolysis of primary carbon–boron bonds was previously observed by K. J. Murray, Ph.D. Thesis, Purdue University.

[8] D. K. Shumway and J. D. Barnhurst, *J. Org. Chem.*, **29**, 2320 (1964).

[9] Research assistant on funds provided by the Southern Utilization Research and Development Division of the U. S. Department of Agriculture (Contract No. 12-14-100-7152(72)) and the National Institutes of Health (5 ROI-GM-10937).

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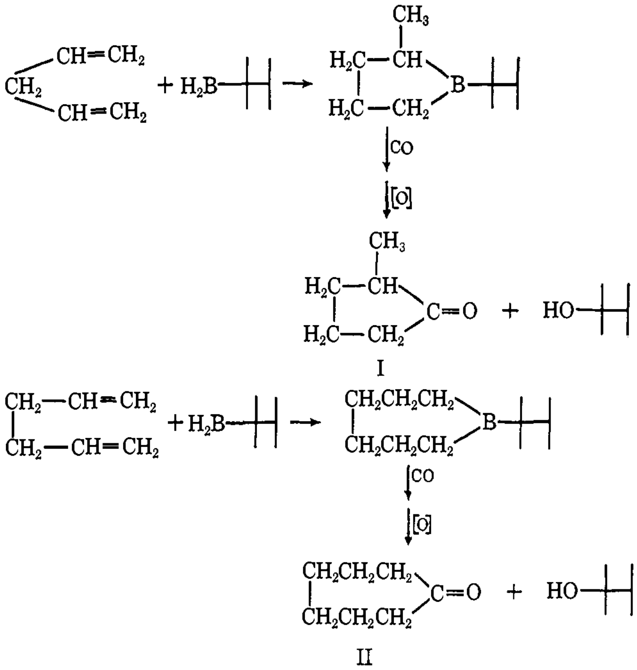
Carbonylation of the Organoboranes from the Cyclic Hydroboration of Dienes with Thexylborane. A Simple Procedure for the Conversion of Dienes into Cyclic Ketones

Sir:

Our recent studies on the carbonylation of trialkylboranes indicate that the alkyl groups are transferred intramolecularly from boron to carbon[1] and that the migratory aptitude of a tertiary alkyl group, such as the thexyl (2,3-dimethyl-2-butyl) group, is much lower than that of primary or secondary groups.[2] This suggested that the 1-thexylboracyclanes and related derivatives produced in the cyclic hydroboration of dienes with thexylboranes[3] should be transformed by carbonylation–oxidation into the corresponding ketones (I, II).



In fact the procedure works very satisfactorily. In two cases we isolated the cyclic organoborane by distillation prior to carbonylation. However, there appears to be no advantage to such prior isolation. Direct carbonylation of the crude solution resulting from the cyclic hydroboration procedure[3] proved to be entirely satisfactory.

In this way isoprene was converted into 3-methylcyclopentanone and 1,4-pentadiene into 2-methylcyclopentanone. 2,3-Dimethylbutadiene yielded a 69:31 mixture of *cis*- and *trans*-3,4-dimethylcyclopentanones. 1,5-Hexadiene yielded cycloheptanone predominantly, with a minor amount of 2,5-dimethylcyclopentanone.

The results are summarized in Table I.

Table I. Cyclic Ketones from Dienes *via* Hydroboration–Carbonylation–Oxidation

Reactant	Ketone yield %,[a]	Ketone products (%)
1-Thexyl-3-methylboracyclopentane	86	3-Methylcyclopentanone (100)
Isoprene	46	3-Methylcyclopentanone (100)
2,3-Dimethyldiene	69	*cis*-3,4-Dimethylcyclopentanone (69) *trans*-3,4-Dimethylcyclopentanone (31)
1,4-Pentadiene	75	2-Methylcyclopentanone (81) Cyclohexanone (19)
1,5-Hexadiene	80	Cycloheptanone (78) 2-Methylcyclohexanone (1) 2,5-Dimethylcyclopentanone (21)
1-Vinylcyclohexene	66[b]	*trans*-1-Hydrindanone (100)

[a] By glpc. [b] Isolated: 60%.

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[1] H. C. Brown and M. W. Rathke, *J. Am. Chem. Soc.*, **89**, 4528 (1967).

[2] H. C. Brown and E. Negishi, *ibid.*, **89**, 5285 (1967).

[3] H. C. Brown and C. D. Pfaffenberger, *ibid.*, **89**, 5475 (1967).